NASA-CR-199654

Cooperative Agreement NCC3-317

# *INTERCALATION OF GRAPHITE FIBERS FOR SPACE POWER APPLICATIONS*

Annual Report

September 1, 1994 - October 13, 1995

submitted to

NASA LEWIS RESEARCH CENTER



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(NASA-CR-199654) INTERCALATION OF GRAPHITE FIBERS FOR SPACE POWER APPLICATIONS Annual Report, 1 Sep. 1994 - 13 Oct. 1995 (Manchester Coll.) 4 p

N96-70368

Unclas

Z9/24 0077305

## INTRODUCTION

The close of the second year of the Cooperative Agreement between NASA Lewis Research Center and Manchester College witnesses a thriving relationship which has been beneficial to both institutions. Collaborative efforts have yielded three publications and substantial progress in a number of directions. This has been accomplished at minimal cost, and has provided important educational opportunities for the students involved. Manchester regards the program as an unqualified success.

## PROGRESS ON RESEARCH EFFORTS

Research has progressed in four basic areas: the kinetics of bromine intercalation of graphite fibers, the radiation shielding ability of intercalated graphite fiber composites, the scale up and optimization of ferric chloride intercalated fibers, and the reduction of ferric chloride to elemental iron in intercalated graphite fibers. The status of each of these projects will be discussed below.

The effort to elucidate kinetics of bromine intercalated graphite fibers has drawn to a close. After two years of effort, the process is not much better understood than it was at the beginning. It had earlier been established that high temperatures inhibit intercalation and low temperature facilitate it.[1] The temperature dependence of the kinetics, however, was unknown. Two tactics were employed in an attempt to determine this. The first involved *in situ* monitoring of the resistance of a graphite fiber during the intercalation process. The technique had been employed in the past at room temperature with success by Gaier for a variety of graphite fiber types.[2] However, when the technique was expanded to include varying the temperature, unsolvable problems developed. The electrical measurements were highly unstable in the bromine atmosphere. Once the fibers were removed from the bromine, the resistance returned to reasonable values. In an attempt to deal with this problem a technique was employed dubbed "interrupted intercalation". In this series of experiments the intercalation progressed was monitored by removing the fiber from the bromine at short intervals and measuring its resistance. This adds a complicating factor because the bromine degasses from the surface of the fiber once it is removed, so the surface of the fiber experienced many intercalation-deintercalation cycles. The final conclusion of these studies was that the fiber to fiber variations had more effect on the reaction rate than did the temperature changes over the range we investigated, which was the liquid range of bromine (266 - 332 K). These results were presented in a poster at the 22nd Biennial Conference on Carbon held in San Diego in July of 1995.[3]

The second effort involved the determination of the effect on intercalation on the

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[1] J.R. Gaier, A. Moinuddin, and J. Terry, *"Kinetic Studies of the Bromine Intercalation of Pitch-Based Graphite Fibers"*, 21st Biennial Conference on Carbon: Expended Abstracts (1993) 578.

[2] J.R. Gaier, *Synthetic Metals 22* (1987) 15.

[3] J.R. Gaier, J.R.T. Bunch, and W.C. Hardebeck, *"Temperature Dependence of the Intercalation of Bromine Into Pitch-Based Fibers"*, 22nd Biennial Conference on Carbon: Extended Abstracts (American Carbon Society, St. Marys, PA, 1995) 666.

radiation shielding ability of graphite-epoxy composites. This was done in two phases. The first involved monitoring the intensity of the 13 keV x-ray and the 46.5 keV $\gamma$-ray from a $^{210}Pb$ source as the thickness of composite was varied. Pristine graphite fiber composites were compared with aluminum composites made with fibers intercalated with $Br_2$. These results indicated that the intercalated composites provided shielding from x-rays and $\gamma$-rays comparable to that provided by aluminum. This work was presented at the International SAMPE Conference in Parsippany, NJ in 1994.[4] This study was expanded to include the effect of shielding with a higher Z intercalate, IBr. This analysis showed that the mass absorption coefficient for IBr intercalated composites was three times that of aluminum, conferring a significant advantage in weight sensitive applications where shielding from high energy electromagnetic radiation is important. These results were presented at the 22nd Biennial Conference on Carbon held in San Diego in July of 1995.[5]

The optimization and scale up of $FeCl_3$ intercalation of graphite fibers is the focus of the third effort in the agreement. A statistical design of experiments was used to optimize a vapor phase intercalation reaction with pitch-based P-100 fibers, with the variables time, temperature, and the difference in temperature between the intercalate zone and the graphite zone of a tube furnace. Resistivity data from a suite of experiments were used to generate a response surface which guided the next suite of experiments. Three suites of experiments lead to optimum conditions of a temperature between 350 and 365 °C, a time of 14 to 18 hours, and a temperature difference of 20 to 35 °C. The response surface in this region was flat compared to fiber to fiber variations. These results were reported at the 22nd Biennial Conference on Carbon held in San Diego in July of 1995.[6] Optimization has been initiated using vapor grown graphite fibers. Scale-up has been postponed until the optimum fiber for the reduction to Fe intercalated fibers has been determined.

The final effort within the agreement was to reduce the $FeCl_3$ within the intercalated fibers to Fe metal without deintercalating the fibers. The original designed called for electrochemical intercalation, but the equipment for this (which was to be supplied by NASA) has not yet been received. Since the work is predicated on the success of this phase of the research, it was decided to try to reduce the fibers using wet chemical methods. This reduction was done using the method of Yazami[7] which utilized n-butyl lithium as the the reducing agent. X-ray diffraction analysis done at NASA LeRC by Dr. Gaier indicates that the reduction was successful, assuming that the lattice parameter reported in the literature are correct. Magnetic susceptibility measurements carried out by Dr. Hambourger at Cleveland State University,

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[4]J.R. Gaier and J. Terry, *"EMI Shields Made From Intercalated Graphite Composites"*, Electronic Materials and Processes for a Peace Time World (Society for the Advancement of Material and Process Engineering, Covina, CA, 1994) 221. Also, NASA Technical Memorandum 106979, 1995.

[5]J.R. Gaier, J.R.T. Bunch, and M.L. Davidson, *"Effect of Intercalation on the Ionizing Radiation Shielding of Graphite Fiber Composites"*, 22nd Biennial Conference on Carbon: Extended Abstracts (American Carbon Society, St. Marys, PA, 1995) 662.

[6]J.R. Gaier, J.A. Walker, and Y.R. Yoder, *"Optimization of the Iron (III) Chloride Intercalation of Graphite Fibers"*, 22nd Biennial Conference on Carbon: Extended Abstracts (American Carbon Society, St. Marys, PA, 1995) 668.

[7]R. Yazami, *Synthetic Metals **20** (1987) 383.*

however indicate that the material is not ferromagnetic. It is not clear whether this can be altered by using the electrochemical technique or a different fiber type. That will be the focus of upcoming work.

Since the initiation of the grant we have employed four students half-time, and published four papers. Given the modest level of the funding we are very pleased with these results, and hope to maintain a long continuing relationship with NASA.